Abstract:

Stable waterborne acrylated alkyd dispersions comprising amine neutralized acrylic modified said selective alkyd resins, and a process for manufacturing said resins and dispersions involving said resin thus finding its end use and application in variety of coating/paint formulations. Said selective alkyd resin facilitates a stable aqueous dispersion comprising amine neutralized dispersions of acrylate-modified alkyd resins with very low organic solvent demands so as to formulate VOC (volatile organic compound) compliant coatings out of the same with desired VOC target values optionally containing other ingredients to further benefit/boost the attributes of the dispersion adapted for coating/paint compositions. Said dispersions obtained of said selective alkyd resins in also being free of emulsifiers exhibits good water resistance, has high storage stability, long shelf life, high shear stability without formation of any aggregates and is suitable for its end use and application in high quality glossy air drying and stoving applications.
FIELD OF THE INVENTION

The present invention particularly relates to selective alkyd resins, and more particularly, relates to stable waterborne acrylated alkyd dispersions comprising amine neutralized acrylic modified said selective alkyd resins, and a process for manufacturing said resins and dispersions to find its end use and application in variety of coating/ paint formulations. More particularly, said selective alkyd resin facilitates a stable aqueous dispersion comprising amine neutralized dispersions of acrylate-modified alkyd resins with very low organic solvent demands so as to formulate VOC (volatile organic compound) compliant coatings out of the same with desired VOC target values and optionally contains other ingredients -to further benefit/ boost the attributes of the dispersion adapted for coating/ paint compositions. Advantageously, said dispersions obtained of said selective alkyd resins in also being free of emulsifiers exhibits good water resistance, has high storage stability, long shelf life, high shear stability without formation of any aggregates and is suitable for its end use and application in high quality glossy air drying and stoving applications.

BACKGROUND OF THE INVENTION

Environmental concern has become increasingly important in recent years. This concern not only extends to preservation of the environment for its own sake, but extends to safety for the public as to both living and working conditions. Volatile organic emissions resulting from coating compositions which are applied and used by industry and by the consuming public are often not only unpleasant, but may contribute to photochemical smog. Fire and health hazards of organic solvents also are well known. Regulations to limit the amount of volatile organic compound (VOC) content of industrial coatings have encouraged research and development to explore new technologies directed at reducing solvent emissions from industrial solvent-based coatings operations such as automotive, appliance, general metal, furniture, and the like. One technology involves the replacement of organic solvents with water and is of particular interest for the obvious reasons of availability, cost, and environmental acceptability. However, while the move from organic solvent-based compositions to aqueous compositions brings health and safety benefits, aqueous coating compositions must meet or exceed the performance standards expected from solvent-based compositions. The need to
meet or exceed such performance standards places a premium on the characteristics and properties of waterborne polymer dispersions used in aqueous coating compositions.

Coating materials, more particularly paints and varnishes, have for a long time been prepared synthetically. Many of these coating materials are based on what are called alkyd resins, which in general are prepared using polybasic acids, alcohols and fatty acids and/or fatty acid derivatives. One particular group of these alkyd resins form cross-linked films on exposure to oxygen, the cross-linking taking place by oxidation with involvement of unsaturated groups. However, while alkyd resins have shown, and continue to show, promise, they have relatively long period of time for drying. Dispersions of acrylate polymers, although drying more quickly, do need co-solvents for effective film formation. Acrylic-modified alkyd resins combine the two advantages of the individual components without the need to tolerate their disadvantages. It is therefore very important economically and technically to carry out further development of these alkyd resins in particular in the sense discussed above.

In recent years, more attention has been given to water-dispersible alkyd resins since the organic solvent content can be reduced remarkably in comparison to water-soluble alkyd resins. For producing the water-dispersible alkyd resins, there are prior established known methods for emulsifying and dispersing by using an emulsifier, and a method for self-dispersing by imparting emulsifiability to the alkyd resin itself by incorporating hydrophilic groups such as carboxylic acids and thereby neutralising with amines. The dispersing method by using an emulsifier can hardly be used practically since water resistance is reduced remarkably due to bad influence of the emulsifier.

Many prior patents disclose methods to obtain water-dissipatable polyesters by neutralizing residual or unreacted carboxylic acid groups on the polymer with ammonia or various organic amines.

U.S. 3,666,698 relates to an alkyd resin prepared by reacting an oil containing an olefinically unsaturated carboxylic fatty acid having at least 10 carbon atoms, with more than 30 percent but less than 45 percent of phenylindanedicarboxylic acid and a sufficient amount of a trihydroxy polyol to provide an OH:COOH ratio in the range from about 1.5 to about 2.5 and a sufficient quantity of a benzene tribasic acid or anhydride to react with from 70 to about 80 percent of the
hydroxy groups present to form a water-dispersible alkyd resin capable of air
drying to a hard, glossy, durable finish without baking.

U.S. 3,699,066 relates to electro deposition type resins but not limited to alkyds,
epoxy, phenolic, alkyd-amino combinations, amino resins, acrylics, polyesters,
trimellitic anhydride condensates and particularly, relates to the stabilizers such
as in the bath during the electro deposition process prevents the build up of the
ammonia of amine, including alkanolamine, which was used to neutralize the
resin thus establishing the benefit of certain hydroxy functional amines for
neutralization.

U.S. 3,549,577 relates to water soluble, polyester resin base baking vehicles
which are fast curing at relatively low temperatures wherein the vehicles are
prepared by partially pre-curing in an aqueous medium polyester pre-polymer
with an alkylated polymethylol melamine crosslinking agent.

U.S. 3,494,882 is directed to a water reducible paint capable of forming a high
gloss coating which comprises an initial emulsion in water based on initial
emulsion of an air drying unsaturated fatty acid modified polyester said polyester
having an acid value of 0-30 and being insoluble in ammonia or amine water, a
non-ionic or anionic surfactant, pigments dispersed in the initial emulsion,
polymeric synthetic latex prepared by polymerization of ethylenically unsaturated
monomers in water in the presence of free radical producing surfactants and
blended with said initial emulsion and pigments. Said polymeric latex being
already in a copolymerized state cannot be said to have any kind of covalent
interaction between the alkyd resin and the acrylic group.

U.S. 3,434,987 relates to aqueous stoving varnishes based on amine salts of
semiesters of hydroxy group containing fatty acid modified alkyd resins
comprising salts of semiesters of water insoluble alkyd resins, which does not
teach any acrylic modification of the alkyd resin.

U.S. 3,345,313 is based on the preparation of alkyd resins involving heating a
reaction mixture comprising polyhydric alcohol and polycarboxylic acid, the
improvement comprising the steps including in said reaction mixture at least one
polymethylolalkanoic acid selected from the group consisting of trimethylolacetic
acid and dimethylolalkanoic acid.
Alkyd resins with high oil length C-18 fatty acid groups are commercially available for use in manufacturing water-dissipatable paints. However, due to their oil-like or hydrophobic properties, alkyds require organic co-solvents for preparing satisfactory dispersions. The amount of solvent required is not insignificant with 1 pound or more of solvent per 3 pounds of alkyd resin being typical. Such high solvent demand makes it difficult to formulate compliant coatings with VOC target values.

US4720522 describes water reducible alkyd vinyl copolymer resins. The copolymer dispersions are prepared using, more particularly, copolymers obtained by solution polymerisation of (metha) acrylates and unsaturated fatty acids. These copolymers requires large amount of solvents for processing and there after to obtain the dispersions. Removal of such high amounts of solvents from dispersions can create safety and economic problems.


The use of resin dispersions with controlled particle size distributions is gaining more and more attention because the controlled particle size distribution helps to control rheology, minimizes solvent usage, and controls viscosity and property of the resin dispersion.

US patent application US2005/0004272A1 discloses the small particle latex compositions based on waterborne alkyd seeds. The compositions are prepared by emulsion polymerisation. These latexes show the particle size in the range of 60-140 nm. The advantage of such low particle size latexes are in terms of gloss and film forming properties, film clarity and porous substrate penetration. However, the disadvantage is that high amount of resin penetration in to the porous substrates due to small particle size which ultimately reduces gloss and softness of the coat.

Thus as apparent from the abovesaid, there is a longfelt need in the art to provide for acrylate modified alkyd resins and waterborne acrylated alkyd dispersions involving said resins, which while on one hand in involving the alkyd resin may advantageously form cross-linked film on exposure to oxygen would
also have modified drying time corrected by acrylic modification of the said resin. Further to the aforesaid, it is also imperative to provide for said acrylate modified selective alkyd resins that are water soluble/ water-dispersible and substantially free of organic solvent content by so as to remarkably reduce the organic solvent content while formulating coatings involving the same with desired VOC target values, which in addition would-be favourably emulsifiable due to incorporation of suitable hydrophilic groups to be self dispersing in the complete absence of any emulsifier that tends to sacrifice water resistance properties of said resin.

OBJECTS OF THE INVENTION

It is thus a primary object of the present invention to provide for selective alkyd resins that may be acrylate modified to provide for stable waterborne acrylated alkyd dispersions to facilitate the formulation of coating/ paint compositions comprising the same thus favouring reduced VOC (volatile organic compound) content of the compositions also adapted for good gloss on both porous and non-porous substrates.

It is another object of the present invention to provide for a process of manufacturing said selective alkyd resins that may be acrylate modified and stable waterborne dispersions and coating/ paint compositions involving the same, which process would be simple and facile involving one pot reaction wherein it would no longer be necessary to strip organic solvents from said dispersions once formed.

It is another object of the present invention to provide for said selective alkyd resins that may be acrylate modified and stable waterborne dispersions and coating/ paint compositions involving the same with broader particle size distribution (bi-model) for enhanced properties both on porous and non porous substrates.

It is another object of the present invention to provide for said selective alkyd resins that may be acrylate modified and stable waterborne dispersions of said selective alkyd resins that is amine neutralized that would impart emulsifiability in the absence of any emulsifiers so as to avoid sacrificing water resistance properties of the said resin.
It is yet another object of the present invention to provide for said selective alkyd resins that may be acrylate modified and stable waterborne dispersions coating/paint compositions comprising the same with low organic solvent demands so as to formulate VOC compliant coatings out of the same with desired VOC target values with less VOC emission particularly, required for hospitals, hotels etc. that would eventually be environmentally friendly, which in addition would also have low odour and hence easy for the painter to do his job.

It is another object of the present invention to provide for said selective alkyd resins that may be acrylate modified and stable waterborne dispersions coating/paint compositions comprising the same such that any spillage of paint, hands and other painting accessories can be washed with water or soap water thus eliminating the need of solvents for the washing the same thus reducing usage of solvents and hence low VOC emissions at application site.

It is still another object of the present invention to provide for said stable waterborne dispersions with high storage stability, long shelf life, high shear stability without formation of any aggregates.

It is another object of the present invention to provide for said dispersions to find its end use and application in coating/paint formulations for high quality glossy air drying and stoving applications.

It is yet another object of the present invention to provide for said selective alkyd resin based dispersions with controlled and broad particle size distributions to aid rheology control, minimize solvent usage, and control viscosity and property of the resin dispersion.

**SUMMARY OF THE INVENTION**

Thus according to the basic aspect of the present invention there is provided an alkyd resin comprising a polycondensed product obtained of

(a) about 40 to 80 weight percent of a vegetable oils or monobasic fatty acid,
(b) about 10 to 30 weight percent of a glycol or polyl,
(c) about 3 to 10 weight percent of a polyoxyethylene glycol,
(d) about 10 to 40 weight percent of a polycarboxylic acid.
It is thus surprisingly found by way of the present invention that when selective polyoxyethyleneglycol reacts with alkyd based precursors involving vegetable oils or monobasic fatty acid, glycol or polylol, and polycarboxylic acid, the same provides for alkyd resin comprising a polycondensed product with non-ionic segments along the polycondensed product backbone thus enabling a low viscosity by high molecular weight based highly branched resin that is also capable of acrylic modification, which modification is attained in presence of acrylics that is substantially free of co-solvents for attaining a waterborne acrylated alkyd dispersion, which in turn also contributes for increased stability of the resin in the dispersion/ aqueous phase being stable towards pH variations, towards salt additions and increased freeze/thaw stability.

Importantly, it is only when the selective polyoxyethylene glycol reacts with said alkyd based precursors that such alkyd resin comprising a polycondensed product could be achieved having a highly branched structure with low viscosity and high molecular weight, which is capable of modification by co-polymerization in a medium involving acrylics that is substantially free of co-solvents facilitating attainment of a stable waterborne dispersion.

Usually, the prior known acrylic modified alkyd have high molecular weight and is highly hydrophobic and viscous hence to disperse it in to water remains a challenge in the art as such known types of resins and its dispersions gives very high viscosity or very low solids which was circumvented by the present technical advance by employing polyoxyethyleneglycol for polycondensation with alkyd based precursors which unexpectedly facilitates the attainment of alkyd resin comprising a polycondensed product with desired viscosity levels with high solids that eventually provides for the desired stability to the resin in the dispersion/ aqueous phase.

According to a preferred aspect of the present invention there is provided said alkyd resin comprising said polycondensed product having high molecular weight by low viscosity, involving viscosity values ranging from U to Z1 at 25 °C on a Gardner scale with a number average molecular weight ($M_n$) of 1500 to 4000 and weight average molecular wt. ($M_w$) 8000 to 20000 and a final acid value in the range of about 1-10 on solids.
Advantageously, said alkyd resin comprising said polycondensed product has a Gardner-Holdt viscosity in the range of from about W to about Y at about 90.0% non-volatiles in water soluble glycol ether based solvents.

More advantageously said alkyd resin, comprising said polycondensed product is adapted for modification by co-polymerization substantially free of co-solvents and with increased stability towards pH variations, addition of salts and increased freeze/thaw stability.

According to another preferred aspect of the present invention there is provided said alkyd resin comprising said polycondensed product and water soluble glycol ether solvents preferably selected from ethylene glycol monobutyl ether, ethylene glycol monoethyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, propylene glycol methylether, dipropylene glycol methylether, propylene glycol propylether adapted for a storage stability of minimum 1 year.

According to another aspect of the present invention there is provided a process for the preparation of said alkyd resin comprising said polycondensed product comprising the steps of

(a) polycondensing a selective mix comprising about 40 to 80 weight percent vegetable oils or monobasic fatty acid, about 10 to 30 weight percent glycol or polyol, about 3 to 10 weight percent polyoxyethylene glycol, and about 10 to 40 weight percent of polycarboxylic acid at reaction temperature of upto 245°C;
(b) continuing the polycondensation reaction until a final acid value of the resultant alkyd resin of from about 1-10 on solids is reached.

According to another preferred aspect of the present invention there is provided said process wherein said step (b) comprises the steps of

(i) polycondensing the selective mix to an acid number in the range of 15 to 60 mg-KOH/g preferably 31 mg-KOH/g initially in the temperature range of 200°C to 260°C preferably 238°C over a period of 1 to 4 hours preferably 2 hours;
(ii) attaining a maximum temperature preferably 245°C at the acid value of preferably 4.5;
(iii) continuing the condensation reaction until the attainment of acid value in the range of 1 to 10 mg-KOH/g preferably 2.9 that is followed by cooling to discharge the resultant alkyd resin that is clear and free from suspended matters with non
volatiles in the range of 90 to 100% preferably 97.1% and having a final acid value in the range of 1 to 10 mg-KOH/g preferably 2.5 mg-KOH/g.

According to yet another aspect of the present invention there is provided a waterborne acrylated alkyd dispersion comprising amine neutralized acrylic modified alkyd resin involving
(a) about 40 to 80 weight percent of a vegetable oils or monobasic fatty acid,
(b) about 10 to 30 weight percent of a glycol or polyol,
(c) about 3 to 10 weight percent of a polyoxyethylene glycol,
(d) about 10 to 40 weight percent of a polycarboxylic acid;
(e) about 15-40 weight percent at least one acrylic based unsaturated carboxylic acid and at least one acrylate based carboxyl-free olefinically unsaturated monomer.

According to yet another aspect of the present invention there is provided a waterborne acrylated alkyd dispersion comprising amine neutralized acrylic modified alkyd resin obtained of copolymerizing
(i) about 15-40 weight percent of at least one acrylic based unsaturated carboxylic acid and at least one acrylate based carboxyl-free olefinically unsaturated monomer; in presence of
(ii) polycondensed product involving (a) about 40 to 80 weight percent of a vegetable oils or monobasic fatty acid, (b) about 10 to 30 weight percent of a glycol or polyol, (c) about 3 to 10 weight percent of a polyoxyethylene glycol, (d) about 10 to 40 weight percent of a polycarboxylic acid.

Advantageously, said waterborne acrylated alkyd dispersion is provided having a low VOC (volatile organic compound) content of less than 8% and broader particle size distribution (bi-model) of 50-1000 nm.

More advantageously, said waterborne acrylated alkyd dispersion is provided having a Gardner-Holdt viscosity in the range of from about Z1 to about Z5, at 40-50% non-volatiles at room temperature and a number average molecular weight (Mn) of 3000-4500 and weight average molecular wt. (Mw) 30000-50000.

Preferably said waterborne acrylated alkyd dispersion is provided comprising about 10-40% of particle having average particle size in the range of about 350-600nm, and about 60-90% of particles having average particle size in the range of about 30-200 nm.
Advantageously, said waterborne acrylated alkyd dispersion is provided that is substantially free of volatile organic solvents and exhibits a long shelf life and storage stability for 30 days at 55 °C, a high shear stability of up to 3000 rpm speed virtually with no aggregate formation, high wet-film stability of 18 hours, increased open time of 30-45 minutes and wherein dispersions with particle sizes even up to 1 µm remains stable and free from gel specks despite being substantially free from organic solvents.

According to another preferred aspect of the present invention there is provided said waterborne acrylated alkyd dispersion wherein said at least one acrylic based unsaturated carboxylic acid is preferably methacrylic acid and at least one acrylate based carboxyl-free olefinically unsaturated monomer is preferably selected from methyl methacrylate, butylmethacrylate, ethylmethacrylate, tertiarybutylmethacrylate, isobutylmethacrylate, hydroxyethylmethacrylate, hydroxypropylmethacrylate.

Preferably, said waterborne acrylated alkyd dispersion is provided comprising monobasic fatty acid selected from the formulas represented hereunder:

\[
\begin{align*}
\text{R} & = \text{Linoleic} \\
\text{R} & = \text{Linolenic} \\
\text{R} & = \text{Oleic}
\end{align*}
\]

and includes sunflower oil, canola oil, dehydrated castor oil, coconut oil, corn oil, cottonseed oil, fish oil, linseed oil, oiticica oil, soya oil, and tung oil, animal grease, castor oil, lard, palm kernel oil, peanut oil, perilla oil, safflower, tallow oil, walnut oil and are preferably selected from fatty acid components of oil or fatty acids.
including oil derived fatty acids of tallow acid, linoleic acid, linolenic acid, oleic acid, soya acid, myristic acid, linseed acid, crotonic acid, versatic acid, coconut acid, tall oil fatty acid, rosin acid, neodecanoic, neopentanoic, isostearic, 12-
hydroxyxystearic, cottonseed acid with linoleic, linolenic more preferably oleic.

More preferably, said waterborne acrylated alkyd dispersion is provided comprising glycol or polyl including aliphatic, alicyclic, and aryl alkyl glycols and are preferably selected from ethylene glycol; propylene glycol; diethylene glycol; triethylene glycol; tetraethylene glycol; pentaethylene glycol; hexaethylene glycol; heptaethylene glycol; octaethylene glycol; nonaethylene glycol; decaethylene glycol; 1,3-propanediol; 2,4-dimethyl-2-ethyl-hexane-1,3-diol; 2,2-dimethyl-l,2-propanediol; 2-ethyl-2-butyl-1,3-propanediol; 2-ethyl-2-isobutyl-1,3-propanediol; 1,3-butanediol; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; 2,2,4-
tetramethyl-1,6-hexanediol; thiadiethanol; 1,2-cyclohexanediethanol; 1,3-cyclohexanediethanol; 1,4-cyclohexanediethanol; 2,2,4-trimethyl-1,3-pentanediol; 2,2,4-tetramethyl-l,3-cyclobutanediol; p-xylenedi hydroxypivalyl hydroxypivalate; 1,10-decanediol; hydrogenated bisphenol A; tri methylolpropane; trimethylollethane; pentaerythritol; erythritol; threitol; dipentaerythritol; sorbitol; glycerine; trimellitic anhydride; pyromellitic dianhydride; dimethylolpropionic acid.

According to another preferred aspect of the present invention there is provided said waterborne acrylated alkyd dispersion comprising polyoxyethylene glycol selected from polyoxyethylene glycol 400, polyoxyethylene glycol 600, polyoxyethylene glycol 1000, polyoxyethylene glycol 2000.

Preferably said waterborne acrylated alkyd dispersion is provided comprising polycarboxylic acid selected from isophthalic acid, terephthalic acid, phthalic anhydride(acid), adipic acid, tetrachlorophthalic anhydride, dodecanedioic acid, sebacic acid, azelaic acid, 1,4-cyclohexanedicarboxylic acid, 1,3-
cyclohexanedicarboxylic acid, maleic anhydride, fumaric acid, succinic anhydride(acid), 2,6-naphthalenedicarboxylic acid, glutaric acid and esters thereof.

In yet another preferred aspect of the present invention there is provided said waterborne acrylated alkyd dispersion that is amine neutralized with volatile amines to form salts selected from primary amines including ethyl amine, propyl amine, butyl amine, isoamyl amine, amyl amine, hexyl amine, heptyl amine and ethanol amine; secondary amines including diethyl amine, ethyl ethanol amine,
and morpholine; and tertiary amines including dimethylethanolamine, trimethylamine, triethylamine and N-methyl morpholine.

According to another aspect of the present invention there is provided a process for the preparation of said waterborne acrylated alkyd comprising said amine neutralized acrylic modified alkyd resin comprising reacting
(a) about 40 to 80 weight percent of a vegetable oils or monobasic fatty acid,
(b) about 10 to 30 weight percent of a glycol or polyol,
(c) about 3 to 10 weight percent of a polyoxyethylene glycol,
(d) about 10 to 40 weight percent of a polycarboxylic acid; and
(e) about 15-40 weight percent at least one acrylic based unsaturated carboxylic acid and at least one acrylate based carboxyl-free olefinically unsaturated monomer; and obtaining therefrom said waterborne acrylated alkyd dispersion.

According to another aspect of the present invention there is provided a process for the preparation of a waterborne acrylated alkyd dispersion comprising amine neutralized acrylic modified alkyd resin comprising the steps of:

(I) providing said alkyd resin comprising said polycondensed product involving (a)
about 40 to 80 weight percent of a vegetable oils or monobasic fatty acid,
(b) about 10 to 30 weight percent of a glycol or polyol,
(c) about 3 to 10 weight percent of a polyoxyethylene glycol,
(d) about 10 to 40 weight percent of a polycarboxylic acid; 
(II) copolymerizing at least one acrylic based unsaturated carboxylic acid and at least one acrylate based carboxyl-free olefinically unsaturated monomer premixed with a free radical initiator in the presence of said alkyd resin of step (I) and neutralizing with amine; to finally obtain therefrom said waterborne acrylated alkyd dispersion.

According to another preferred aspect of the said process said copolymerization step (II) preferably comprises the steps of:
(i) premixing at least one acrylate based carboxyl-free olefinically unsaturated monomer involving non-carboxylic acid vinyl monomers and at least one acrylic based unsaturated carboxylic acid involving vinyl carboxylic acid preferably methacrylic acid with a free radical initiator;
(ii) slowly adding the premix to the selective alkyd in ratios ranging from 85:15 to 70:30 in the temperature range of about 130-140°C for a time period of 1 - 4 hrs preferably 2 hrs for a high degree of conversion of said non-carboxylic acid vinyl
and vinyl carboxylic acid monomers so as to reach to the copolymer acid value of 30-60 on solids;

(iii) neutralizing the carboxylic acids end groups with various amines followed by thinning with water to obtain said waterborne acrylated alkyd dispersion.

According to another aspect of the present invention there is provided a coating/paint composition comprising alkyd resin involving a polycondensed product obtained of

(a) about 40 to 80 weight percent of a vegetable oils or monobasic fatty acid,
(b) about 10 to 30 weight percent of a glycol or polyol,
(c) about 3 to 10 weight percent of a polyoxyethylene glycol,
(d) about 10 to 40 weight percent of a polycarboxylic acid.

According to another aspect of the present invention there is provided a coating/paint composition comprising a waterborne acrylated alkyd dispersion comprising amine neutralized acrylic modified alkyd resin involving

(a) about 40 to 80 weight percent of a vegetable oils or monobasic fatty acid,
(b) about 10 to 30 weight percent of a glycol or polyol,
(c) about 3 to 10 weight percent of a polyoxyethylene glycol,
(d) about 10 to 40 weight percent of a polycarboxylic acid;
(e) about 15-40 weight percent at least one acrylic based unsaturated carboxylic acid and at least one acrylate based carboxyl-free olefinically unsaturated monomer.

According to yet another aspect of the present invention there is provided a coating/paint composition comprising waterborne acrylated alkyd dispersion comprising amine neutralized acrylic modified alkyd resin obtained of copolymerizing

(I) at least one acrylic based unsaturated carboxylic acid and at least one acrylate based carboxyl-free olefinically unsaturated monomer premixed with a free radical initiator; in presence of

(II) alkyd resin comprising polycondensed product involving (a) about 40 to 80 weight percent of a vegetable oils or monobasic fatty acid,
(b) about 10 to 30 weight percent of a glycol or polyol,
(c) about 3 to 10 weight percent of a polyoxyethylene glycol,
(d) about 10 to 40 weight percent of a polycarboxylic acid.
Advantageously said coating/paint composition of the present invention in having low VOC content of less than 8% and broader particle size distribution (bimodel) of 50-1000 nm favours gloss on both porous and non-porous substrates; slow drying for high gloss for brush applications.

According to another aspect of the present invention there is provided a commercial or industrial material, a structure or building or a substrate both porous and non-porous comprising said coating/paint composition having low VOC content of less than 8% and broader particle size distribution (bimodel) of 50-1000 nm favouring gloss on both porous and non porous substrates.

According to yet another aspect of the present invention there is provided a method of coating/painting a commercial or industrial material, a structure or building or a substrate both porous and non-porous comprising selectively applying said coating/paint composition to at least a portion of commercial or industrial material, a structure or building or a substrate requiring low VOC (volatile organic compound) content, slow drying and high gloss coats/paints.

The present invention thus provides an amine neutralized stable waterborne acrylic modified alkyd dispersions, having broad particle size distribution in the range of about 50 - 1000 nm. These dispersions are produced by solution polymerization using 15-30 wt% of acrylics, based on the total weight of the alkyd and acrylics, in presence of alkyd using small amounts of solvents that it is no longer necessary to remove them from the dispersions.

The invention relates to acrylic modified alkyd dispersions having about 10-40% of particle having an average particle size in the range of about 350-600nm, and about 60-90% of particles having an average particle size in the range of about 30-200 nm.

In accordance with this invention, said amine neutralized acrylic modified alkyd dispersion comprising

1. At least one alkyd resin comprises reacting:
   1.1 about 45 to 85 weight percent of a vegetable oils or monobasic fatty acid,
   1.2 about 10 to 25 weight percent of a glycol or polyol,
   1.3 about 3 to 10 weight percent of a polyoxyethylene glycol,
1.4 about 10 to 40 weight percent of a polycarboxylic acid, and

2. At least one methacrylic acid and at least one further, carboxyl-free olefinically unsaturated monomer for copolymerisation in presence of 1.

Through the measures according to the invention it is additionally possible to obtain advantages including the following:

The dispersions of the invention preferably contain no substantial volatile organic solvents. Furthermore, dispersions of the invention exhibit a high level of storage stability, a long shelf life, very good storage properties and a very high shear stability. More particularly virtually no aggregate is formed. It is interesting to see that the dispersions of the invention, even with particle sizes of up to 1 µm, were stable and free from gel specks, despite being substantially free from organic solvents. It is further advantage that for their preparation it was possible to do largely without organic solvents requiring removal from the dispersion afterward.

The coating materials of the invention exhibit high wet-film stability and an increased open time.

The dispersions of the invention can be prepared inexpensively on a large scale.

The dispersions of the invention are eco-friendly and can be prepared and processed safely and without great cost and complexity.

DETAILED DESCRIPTION OF THE INVENTION

As discussed hereinbefore the present invention provides for selective alkyd resin comprising a polycondensed product and stable waterborne polymer dispersions involving said alkyds that is capable of acrylic modification and amine neutralization. The present invention also provides for processes for manufacturing the same to find its end use and application in coating/ paint formulations. More preferably, the waterborne acrylated alkyd dispersion comprising amine neutralized acrylic modified selective alkyd resin has very low organic solvent demands to provide for VOC compliant coatings/ paints with desired VOC target values. Said waterborne dispersion in being advantageously free of emulsifiers has good water resistance, has high storage stability, long shelf life, high shear stability without formation of any aggregates and is suitable for its end use and application in high quality glossy air drying and stoving applications.
The present invention thus provides for a selective alkyd resin comprising a polycondensed product obtained of
(a) about 40 to 80 weight percent of a vegetable oils or monobasic fatty acid,
(b) about 10 to 30 weight percent of a glycol or polyol,
(c) about 3 to 10 weight percent of a polyoxyethylene glycol,
(d) about 10 to 40 weight percent of a polycarboxylic acid;

which may be acrylated to provide for a waterborne acrylated alkyd dispersion comprising amine neutralized acrylic modified alkyd resin to find its end use and application in coating/paint compositions.

Said acrylated alkyd resin thus attained is very stable before thinning and can be used as coating resin also. However, since the viscosity of said acrylated alkyd resin is very high due to its high solids (93%) or due to the very low amount of co-solvent content the same is eventually made available as dispersion that exhibits a long shelf life and storage stability for 30 days at 55 °C.

Special and unique characteristics of said acrylated selective alkyds resin are:

1. Processing of resin can be done in a medium that is substantially free of co-solvents, which in turn facilitates to avoid stripping process after the reaction that again leads to time and energy saving, unlike conventional methods and processes.
2. Due to its broad particle size distribution, the dispersion shows very high gloss and DOI (distinct of image) on both porous (ex: wood) and non porous (ex: metal) substrates.
3. Shows excellent wetting with pigments hence no need to add any additional wetting agents in the paint preparation process.
4. It's rheology shows shear thinning behaviour, which results in to ease of application with brush, less efforts need to put for brush application, compared to solvent based system.
5. Shows excellent stability with out phase separation, after the accelerated test at 55°C for 30 days.

Its beneficial attributes to the coating/paint industry involves attainment of low VOC, environmental friendly coatings which in being waterborne during spillage of paint, hands and other painting accessories can be washed with water or soap.
water without involving any solvents for the same and at the same time reduces usage of solvents and hence low VOC emissions at application site. Further to the abovesaid, said selective dispersions of the present invention has low odor, and hence easy for the painter to do the job and is particularly of high demand in places where low odour, or less emission of VOC is required, particularly in places like hospitals, hotels and the like.

Said selective alkyd resin comprising a polycondensed product involves monobasic fatty acid preferably selected from the formula:

![Chemical Structure]

Examples of suitable oils and fatty acids (a) include sunflower oil, canola oil, dehydrated castor oil, coconut oil, corn oil, cottonseed oil, fish oil, linseed oil, oiticica oil, soya oil, and tung oil, animal grease, castor oil, lard, palm kernel oil, peanut oil, perilla oil, safflower, tallow oil, walnut oil. Suitable examples of the fatty acid components of oil or fatty acids by themselves are selected from the following oil derived fatty acids; tallow acid, linoleic acid, linolenic acid, oleic acid, soya acid, myristic acid, linseed acid, crotonic acid, versatic acid, coconut acid, tall oil fatty acid, rosin acid, neodecanoic, neopentanoic, isostearic, 12-hydroxystearic, cottonseed acid with linoleic, linolenic and oleic being more preferred.

The glycol or polyol from (b) is preferably selected from aliphatic, alicyclic, and aryl alkyl glycols. Suitable examples of polyols include: ethylene glycol; propylene glycol; diethylene glycol; triethylene glycol; tetraethylene glycol; pentaethylene
glycol; hexaethylene glycol; heptaethylene glycol; octaethylene glycol; nonaethylene glycol; decaethylene glycol; 1,3-propanediol; 2,4-dimethyl-2-ethylhexane-1,3-diol; 2,2-dimethyl-1,2-propanediol; 2-ethyl-2-butyl-1,3-propanediol; 2-ethyl-2-isobutyl-1,3-propanediol; 1,3-butanediol; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; 2,2,4-tetramethyl-1,6-hexanediol; thiodiethanol; 1,2-cyclohexanediethanol; 1,3-cyclohexanediethanol; 1,4-cyclohexanediethanol; 2,2,4-trimethyl-1,3-pentanediol; 2,2,4-tetramethyl-1,3-cyclobutanediol; p-xylenediol hydroxypivalyl hydroxypivalate; 1,10-decanediol; hydrogenated bisphenol A; trimethylolpropane; trimethylolethane; pentaerythritol; erythritol; threitol; dipentaerythritol; sorbitol; glycerine; trimellitic anhydride; pyromellitic dianhydride; dimethylolpropionic acid and the like.

The polyoxyethylene glycol (c) includes polyoxyethylene glycol 400, polyoxyethylene glycol 600, polyoxyethylene glycol 1000, polyoxyethylene glycol 2000 and the like.

The polycarboxylic acid used in (d) in the process and composition of the present invention is preferably selected from the group consisting of isophthalic acid, terephthalic acid, phthalic anhydride(acid), adipic acid, tetrachlorophthalic anhydride, dodecanedioic acid, sebacic acid, azelaic acid, 1,4-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, maleic anhydride, fumaric acid, succinic anhydride(acid), 2,6-naphthalenedicarboxylic acid, glutaric acid and esters thereof.

The carboxylic acid for acrylic modification of said selective alkyd resin preferably involves methacrylic acid and other carboxyl-free olefinically unsaturated monomers preferably selected from methyl methacrylate, butylmethacrylate, ethylmethacrylate, tertiarybutylmethacrylate, isobutylmethacrylate, hydroxyethylmethacrylate, hydroxypropymethacrylate and like that.

In the preferred form of the invention the alkyd resin is prepared with reaction temperatures not exceeding 245°C. and the alkyd having a final acid value in the range of from about 1 to about 10 on solids. Preferably the product will have a Gardner-Holdt viscosity in the range of from about w to about y at 90.0% non-volatiles in glycol ether solvent. The glycol ether solvents are water soluble solvents, preferably selected from ethylene glycol monobutyl ether, ethylene glycol monoethyl ether, ethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monomethyl ether, propylene glycol methylether, dipropylene glycol methylether, propylene glycol propylether and like that.
In the preferred form of the invention, after the preparation of the alkyd resin, the vinyl resin is prepared in the presence of the alkyd resin, with the non-carboxylic acid vinyl monomers and the vinyl carboxylic acid monomers being premixed with a free radical initiator, the premix then being added into an alkyd. In the preferred forms of the invention, the premix and alkyd then are reacted at about 130-140°C for a period of time which assures a high degree of conversion of non-carboxylic acid vinyl and vinyl carboxylic acid monomers. The prepared copolymer having a final acid value in the range of 30 to 60 on solid basis. The carboxylic acids may be neutralised with various amine followed by thinning with water.

The various volatile amines which may be used to form the salts are: primary amines such as ethyl amine, propyl amine, butyl amine, isoamyl amine, amyl amine, hexyl amine, heptyl amine and ethanol amine; secondary amines such as diethyl amine, ethyl ethanol amine, and morpholine; and tertiary amines such as dimethylethanol amine, trimethyl amine, triethylamine and N-methyl morpholine.

The dispersions of the invention having Gardner-Holdt viscosity in the range of from about Z1 to about Z5, at 40-50% non-volatiles at room temperature and having broad particle size distribution, bi phase model, in the range of about 50 - 1000 nm. The broad particle size distribution or biphase model particle size distribution indicates heterogeneity in the system, polymer populations with respect to particle size.

Spheres of uniform size can be theoretically arranged in different ways. In a closed packing of spheres of the same size, either in face centered cubic or hexagonal closed packing, the maximum volume fraction of the spheres is approximately 74. The interstitial voids in a closed packing of spheres are tetrahedral voids formed by the face-centered packing of four large particles. The small particles population of the resin dispersion can fill the interstitial voids of the large particle population of the resin dispersion, and thereby, the total volume of the combined spheres of both the small particles population and large particles population of the resin dispersion can be increased above the maximum of the closed packing of the large particle dispersion.

These polymer dispersions will impact the rheological properties like flow out of brush marks and distinctness of image (DOI), and can be of use to improve the brush drag and the hiding power of paint. Alternatively, a low amount of alkyd resin can be added to the dispersion with the help of emulsifiers to result in an in-
situ prepared bimodal or multi model particle size distribution to get the advantages.

The following examples are provided to illustrate the invention more fully, however, they should not be interpreted to limit the scope of the invention, that include other variations.

Example 1:

A. Alkyd Preparation

To a reaction kettle equipped with agitator, water separator, thermometer and nitrogen supply, the following reaction mixture was charged into the prepared setup:

<table>
<thead>
<tr>
<th>Alkyd ingredients composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parts</td>
</tr>
<tr>
<td>A</td>
</tr>
<tr>
<td>1 Soya oil fatty acid         24.8</td>
</tr>
<tr>
<td>Dehydrogenated castor oil fatty</td>
</tr>
<tr>
<td>2 acid                       37.2</td>
</tr>
<tr>
<td>3 Pentaerythritol             18</td>
</tr>
<tr>
<td>4 Isophthalic acid            15</td>
</tr>
<tr>
<td>5 Polyethoxypolyol- 1000      5</td>
</tr>
<tr>
<td>6 Dibutyltinoxide             0.08</td>
</tr>
<tr>
<td>7 O-Xylene                   3.5</td>
</tr>
<tr>
<td>8 Butyl acetate              0.5</td>
</tr>
<tr>
<td>Water of reaction             -7.1</td>
</tr>
<tr>
<td>9 reaction</td>
</tr>
<tr>
<td>10 Total                     100</td>
</tr>
</tbody>
</table>

The reaction mixture was polycondensed to an acid number of 31 at a temperature of 238°C over a period of two hours 15 minutes. Thereafter, the reaction mass was attained a maximum temperature of 245°C at the acid value of 4.5. The condensation reaction continued until the acid value reached to around 2.9. The water of reaction was 7.1 ml. The product was allowed to cool then, was discharged from reaction kettle. The resulted alkyd was clear and free from suspended matters with non-volatiles of 97.1% and the final acid value was 2.56. The Gardner-Holdt viscosity was in the range of from about W to about X at 90% non-volatiles (90:10 alkyd/diethyleneglycolmethylether solution). The number
average molecular weight (Mn) was 2739, the weight average molecular (Mw) was 10573, and the polydispersity index (PDI) was 3.86.

B. Preparation of Acrylated alkyd dispersion

Acrylated alkyd dispersion composition given below.

<table>
<thead>
<tr>
<th>Alkyd/acrylic copolymer composition</th>
<th>Parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td></td>
</tr>
<tr>
<td>1 Alkyd (Example 1A)</td>
<td>31.89</td>
</tr>
<tr>
<td>2 Diethyleneglycolmethylether</td>
<td>2.99</td>
</tr>
<tr>
<td>3 Methylmethacrylate</td>
<td>1.19</td>
</tr>
<tr>
<td>4 Methacrylic acid</td>
<td>2.39</td>
</tr>
<tr>
<td>5 n-Butylmethacrylate</td>
<td>4.38</td>
</tr>
<tr>
<td>6 Tertiarybutylperbenzoate</td>
<td>0.29</td>
</tr>
<tr>
<td>7 Triethylamine</td>
<td>2.83</td>
</tr>
<tr>
<td>8 Distilled water</td>
<td>54.04</td>
</tr>
<tr>
<td>9 Total</td>
<td>100</td>
</tr>
</tbody>
</table>

To a reaction kettle equipped with agitator, reflux condenser and thermomether. The alkyd prepared in example 1 and diethyleneglycolmethylether were charged into the reaction kettle then the methacrylic acid, methylmethacrylate and butylmethacrylates were premixed with tertiarybutylperbenzoate. This premix was added to the alkyd solution for about 2 hours time at temperature of 135°C. After all the premix was added, it was heated an additional 1 hour at 135°C, then the temperature was reduced to 75°C. The resulted acrylated alkyd having acid value of about 40 on solids. The acid groups of the resin were neutralised with triethylamine. Thereafter, the resin was thinned with water to achieve Gardner-Holdt viscosity of Z1-Z2. The dispersion pH was 8, solids 39.1%. The number average molecular weight (Mn) was 3848, the weight average molecular (Mw) was 38649, and the polydispersity index (PDI) was 10.04. The dispersions were stable as no separation was observed after keeping the samples at 55°C for 30 days. The average particle size was 468nm with 14.2% of particles and 117nm with 85.8% of particles. The alkyd to acrylic ratio was 80:20.

Example 2

<table>
<thead>
<tr>
<th>Alkyd/acrylic copolymer composition</th>
<th>Parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Alkyd (Example 1A)</td>
<td>27.86</td>
</tr>
<tr>
<td>2 Diethyleneglycolmethylether</td>
<td>2.99</td>
</tr>
<tr>
<td>3 Methylmethacrylate</td>
<td>3.18</td>
</tr>
</tbody>
</table>
The experiment of Example 1 is repeated in all essential details except that the alkyd to acrylic ratio was changed from 80:20 to 70:30 and acid value changed from 40 to 44, on solids. The obtained acrylic-modified alkyd dispersion was having Gardner-Holdt viscosity Z2, Solids 38.6%, and pH around 8. The number average molecular weight (Mn) was 4236, the weight average molecular (Mw) was 102334, and the polydispersity index (PDI) was 24.16. The dispersions were stable as no separation was observed after keeping the samples at 55°C for 30 days. The average particle size was 91nm with 47% of particles and 37.2nm with 53% of particles.

The composition is given below

Example 3

<table>
<thead>
<tr>
<th>Alkyd/acrylic copolymer composition</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Alkyd (Example 1A)</td>
<td>40</td>
</tr>
<tr>
<td>2. Diethyleneglycolmethylether</td>
<td>3.51</td>
</tr>
<tr>
<td>3. Methylmethacrylate</td>
<td>1.11</td>
</tr>
<tr>
<td>4. Methacrylic acid</td>
<td>2.22</td>
</tr>
<tr>
<td>5. n-Butylmethacrylate</td>
<td>4.07</td>
</tr>
<tr>
<td>6. Tertiarybutylperbenzoate</td>
<td>0.28</td>
</tr>
<tr>
<td>7. Triethylamine</td>
<td>2.48</td>
</tr>
<tr>
<td>8. Maxemul 6112/20N</td>
<td>1.85</td>
</tr>
<tr>
<td>9. Distilled water</td>
<td>44.50</td>
</tr>
<tr>
<td>10. Total</td>
<td>100</td>
</tr>
</tbody>
</table>

The experiment of Example 1 is repeated in all essential details except that the alkyd to acrylic ratio was changed from 80:20 to 85:15 and acid value changed from 40 to 32, on solid. The obtained acrylic-modified alkyd dispersion was having Gardner-Holdt viscosity Z3, Solids 45.5%, and pH around 8. The number average molecular weight (Mn) was 3887, the weight average molecular (Mw) was 43667, and the polydispersity index (PDI) was 11.23. The dispersions were stable as no separation was observed after keeping the samples at 55°C for 30
days. The average particle size was 86.4nm with 49.7% of particles, 141nm with 39.9% and 435nm with 10.4% of particles.

It is thus possible by way of the present advancement to provide for a selective alkyd resin that is capable of acrylic modification to thus provide for waterborne dispersions comprising the same, which advantageously favours formulating desired VOC target value coating/ paint compositions. Said dispersions in involving a broader particle size distribution (bi-model) favours high gloss applications on both porous and non porous substrates, and also in being free of emulsifiers also avoid sacrificing water resistance properties of the said resin, which also additionally has high storage stability, long shelf life, high shear stability without formation of any aggregates. Advantageously, said broader particle size distribution of the dispersion also aids rheology control, minimize solvent usage, and control viscosity and property of the resin dispersion.
We Claim:

1. Alkyd resin comprising a polycondensed product obtained of
   (a) about 40 to 80 weight percent of a vegetable oils or monobasic fatty acid,
   (b) about 10 to 30 weight percent of a glycol or polyol,
   (c) about 3 to 10 weight percent of a polyoxyethylene glycol,
   (d) about 10 to 40 weight percent of a polycarboxylic acid.

2. Alkyd resin as claimed in claim 1 comprising said polycondensed product
   having high molecular weight by low viscosity, involving viscosity values ranging
   from U to Z at 25 °C on Gardner scale (at 90% solids in glycol ether) with a
   number average molecular weight \( (M_n) \) of 1500 to 4000 and weight average
   molecular wt. \( (M_w) \) 8000 to 20000 and a final acid value in the range of about 1-
   10 mg-KOH/g on solids.

3. Alkyd resin as claimed in anyone of claims 1 or 2 comprising said
   polycondensed product having a Gardner-Holdt viscosity in the range of from
   about W to about Y at about 90.0% non-volatiles in water soluble glycol ether
   based solvents.

4. Alkyd resin as claimed in anyone of claims 1-3, comprising said polycondensed
   product adapted for modification by co-polymerization substantially free of co-
   solvents and with increased stability towards pH variations, addition of salts and
   increased freeze/thaw stability.

5. Alkyd resin as claimed in anyone of claims 1-4 comprising said polycondensed
   product and water soluble glycol ether solvents preferably selected from ethylene
   glycol monobutyl ether, ethylene glycol monoethyl ether, diethylene glycol
   monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol
   monobutyl ether, propylene glycol methylether, dipropylene glycol methylether,
   propylene glycol propylether adapted for a storage stability of minimum 1 year.

6. A process for the preparation of alkyd resin as claimed in anyone of claims 1-5
   comprising said polycondensed product comprising the steps of
   (a) polycondensing a selective mix comprising about 40 to 80 weight percent
   vegetable oils or monobasic fatty acid, about 10 to 30 weight percent glycol or
   polyol, about 3 to 10 weight percent polyoxyethylene glycol, and about 10 to 40
   weight percent of polycarboxylic acid at reaction temperature of upto 245°C;
(b) continuing the polycondensation reaction until a final acid value of the resultant alkyd resin of from about 1-10 on solids is reached.

7. A process as claimed in claim 6 wherein said step (b) comprises the steps of
   (i) polycondensing the selective mix to an acid number in the range of 15 to 60 mg-KOH/g preferably 31 mg-KOH/g initially in the temperature range of 200 to 260 °C preferably 238°C over a period of 1 to 4 hours preferably 2 hours;
   (ii) attaining a maximum temperature preferably 245°C at the acid value of preferably 4.5;
   (iii) continuing the condensation reaction until the attainment of acid value in the range of 1 to 10 mg-KOH/g preferably 2.9 that is followed by cooling to discharge the resultant alkyd resin that is clear and free from suspended matters with non volatiles in the range of 90 to 100% preferably 97.1% and having a final acid value in the range of 1 to 10 mg-KOH/g preferably 2.5 mg-KOH/g.

8. A waterborne acrylated alkyd dispersion comprising amine neutralized acrylic modified alkyd resin involving
   (a) about 40 to 80 weight percent of a vegetable oils or monobasic fatty acid,
   (b) about 10 to 30 weight percent of a glycol or polyol,
   (c) about 3 to 10 weight percent of a polyoxyethylene glycol,
   (d) about 10 to 40 weight percent of a polycarboxylic acid;
   (e) about 15-40 weight percent at least one acrylic based unsaturated carboxylic acid and at least one acrylate based carboxyl-free olefinically unsaturated monomer.

9. A waterborne acrylated alkyd dispersion comprising amine neutralized acrylic modified alkyd resin obtained of copolymerizing
   (i) about 15-40 weight percent of at least one acrylic based unsaturated carboxylic acid and at least one acrylate based carboxyl-free olefinically unsaturated monomer; in presence of
   (ii) polycondensed product involving (a) about 40 to 80 weight percent of a vegetable oils or monobasic fatty acid, (b) about 10 to 30 weight percent of a glycol or polyol, (c) about 3 to 10 weight percent of a polyoxyethylene glycol, (d) about 10 to 40 weight percent of a polycarboxylic acid.
10. A waterborne acrylated alkyd dispersion as claimed in anyone of claims 8 or 9 which is having a low VOC (volatile organic compound) content of less than 8% and broader particle size distribution (bimodel) of 50-1000 nm.

11. A waterborne acrylated alkyd dispersion as claimed in anyone of claims 8 to 10 having a Gardner-Holdt viscosity in the range of from about Z1 to about Z5, at 40-50% non-volatiles at room temperature and a number average molecular weight \( (M_n) \) of 3000-4500 and weight average molecular wt. \( (M_w) \) 30000-50000.

12. A waterborne acrylated alkyd dispersion as claimed in anyone of claims 8 to 11 comprising about 10-40% of particle having average particle size in the range of about 350-600nm, and about 60-90% of particles having average particle size in the range of about 30-200 nm.

13. A waterborne acrylated alkyd dispersion as claimed in anyone of claims 8 to 12 that is substantially free of volatile organic solvents and exhibits a long shelf life and storage stability for 30 days at 55 °C, a high shear stability of up to 3000 rpm speed virtually with no aggregate formation, high wet-film stability of 18 hrs, increased open time of 30-45 minutes and wherein dispersions with particle sizes even upto 1 pm remains stable and free from gel specks despite being substantially free from organic solvents.

14. A waterborne acrylated alkyd dispersion as claimed in anyone of claims 8 to 13 wherein said at least one acrylic based unsaturated carboxylic acid is preferably methacrylic acid and at least one acrylate based carboxyl-free olefinically unsaturated monomer is preferably selected from methyl methacrylate, butylmethacrylate, ethylmethylacrylate, tertiarybutylmethacrylate, isobutylmethacrylate, hydroxyethylmethacrylate, hydroxypropylmethacrylate.

15. A waterborne acrylated alkyd dispersion as claimed in anyone of claims 8 to 14 comprising monobasic fatty acid selected from the formulas represented hereunder:
Oleic and includes sunflower oil, canola oil, dehydrated castor oil, coconut oil, corn oil, cottonseed oil, fish oil, linseed oil, oiticica oil, soya oil, and tung oil, animal grease, castor oil, lard, palm kernel oil, peanut oil, perilla oil, safflower, tallow oil, walnut oil and are preferably selected from fatty acid components of oil or fatty acids including oil derived fatty acids of tallow acid, linoleic acid, linolenic acid, oleic acid, soya acid, myristic acid, linseed acid, crotonic acid, versatic acid, coconut acid, tall oil fatty acid, rosin acid, neodecanoic, neopentanoic, isostearic, 12-hydroxystearic, cottonseed acid with linoleic, linolenic more preferably oleic.

16. A waterborne acrylated alkyd dispersion as claimed in anyone of claims 8 to 15 comprising glycol or polyol including aliphatic, alicyclic, and aryl alkyl glycols and are preferably selected from ethylene glycol; propylene glycol; diethylene glycol; Methylene glycol; tetraethylene glycol; pentaethylene glycol; hexaethylene glycol; heptaoxyethylene glycol; octaethylene glycol; nonaethylene glycol; decaethylene glycol; 1,3-propanediol; 2,4-dimethyl-2-ethyl-hexane-1,3-diol; 2,2-dimethyl-1,2-propanediol; 2-ethyl-2-butyloxy-1,3-propanediol; 2-ethyl-2-isobutyl-1,3-propanediol; 1,3-butanediol; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; 2,2,4-tetramethyl-1,6-hexanediol; thiodiethanol; 1,2-cyclohexanediol; 1,3-cyclohexanediol; 1,4-cyclohexanediol; 2,2,4-trimethyl-1,3-pentanediol; 2,2,4-tetramethyl-1,3-cyclobutanediol; p-xylenediol hydroxypivalyl hydroxypropionate; 1,10-decanediol; hydrogenated bisphenol A; trimethylolpropane; trimethylolpropane; pentaerythritol; erythritol; threitol; dipentaerythritol; sorbitol; glycerine; trimellitic anhydride; pyromellitic dianhydride; dimethylolpropionic acid.

17. A waterborne acrylated alkyd dispersion as claimed in anyone of claims 8 to 16 comprising polyoxyethylene glycol selected from polyoxyethylene glycol 400,
polyoxyethylene glycol 600, polyoxyethylene glycol 1000, polyoxyethylene glycol 2000.

18. A waterborne acrylated alkyd dispersion as claimed in anyone of claims 8 to 17 comprising polycarboxylic acid selected from isophthalic acid, terephthalic acid, phthalic anhydride(acid), adipic acid, tetrachlorophthalic anhydride, dodecanedioic acid, sebacic acid, azelaic acid, 1,4-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, maleic anhydride, fumaric acid, succinic anhydride(acid), 2,6-naphthalenedicarboxylic acid, glutaric acid and esters thereof.

19. A waterborne acrylated alkyd dispersion as claimed in anyone of claims 8 to 18 that is amine neutralized with volatile amines to form salts selected from primary amines including ethyl amine, propyl amine, butyl amine, isoamyl amine, amyl amine, hexyl amine, heptyl amine and ethanol amine; secondary amines including diethyl amine, ethyl ethanol amine, and morpholine; and tertiary amines including dimethylethanol amine, trimethyl amine, triethylamine and N-methyl morpholine.

20. A process for the preparation of a waterborne acrylated alkyd dispersion as claimed in anyone of claims 8 to 19 comprising said amine neutralized acrylic modified alkyd resin comprising reacting (a) about 40 to 80 weight percent of a vegetable oils or monobasic fatty acid, (b) about 10 to 30 weight percent of a glycol or polyol, (c) about 3 to 10 weight percent of a polyoxyethylene glycol, (d) about 10 to 40 weight percent of a polycarboxylic acid; and (e) about 15-40 weight percent at least one acrylic based unsaturated carboxylic acid and at least one acrylate based carboxyl-free olefinically unsaturated monomer; and obtaining therefrom said waterborne acrylated alkyd dispersion.

21. A process for the preparation of a waterborne acrylated alkyd dispersion comprising amine neutralized acrylic modified alkyd resin as claimed in anyone of claims 8 to 19 comprising the steps of:

(1) providing said alkyd resin comprising said polycondensed product involving (a) about 40 to 80 weight percent of a vegetable oils or monobasic fatty acid, (b) about 10 to 30 weight percent of a glycol or polyol, (c) about 3 to 10 weight percent of a polyoxyethylene glycol,
(d) about 10 to 40 weight percent of a polycarboxylic acid;
(II) copolymerizing at least one acrylic based unsaturated carboxylic acid and at least one acrylate based carboxyl-free olefinically unsaturated monomer premixed with a free radical initiator in the presence of said alkyd resin of step (I) and neutralizing with amine; to finally obtain therefrom said waterborne acrylated alkyd dispersion.

22. A process as claimed in claim 21 wherein said copolymerization step (II) preferably comprises the steps of:
(i) premixing at least one acrylate based carboxyl-free olefinically unsaturated monomer involving non-carboxylic acid vinyl monomers and at least one acrylic based unsaturated carboxylic acid involving vinyl carboxylic acid preferably methacrylic acid with a free radical initiator;
(ii) slowly adding the premix to the selective alkyd in ratios ranging from 85:15 to 70:30 in the temperature range of about 130-140°C for a time period of 1 - 4 hrs preferably 2 hrs for a high degree of conversion of said non-carboxylic acid vinyl and vinyl carboxylic acid monomers so as to reach to the copolymer acid value of 30-60 on solids;
(iii) neutralizing the carboxylic acids end groups with various amines followed by thinning with water to obtain said waterborne acrylated alkyd dispersion.

23. A coating/ paint composition comprising alkyd resin involving a polycondensed product obtained of
(a) about 40 to 80 weight percent of a vegetable oils or monobasic fatty acid,
(b) about 10 to 30 weight percent of a glycol or polyol,
(c) about 3 to 10 weight percent of a polyoxyethylene glycol,
(d) about 10 to 40 weight percent of a polycarboxylic acid.

(a) about 40 to 80 weight percent of a vegetable oils or monobasic fatty acid,
(b) about 10 to 30 weight percent of a glycol or polyol,
(c) about 3 to 10 weight percent of a polyoxyethylene glycol,
(d) about 10 to 40 weight percent of a polycarboxylic acid;
(e) about 15-40 weight percent at least one acrylic based unsaturated carboxylic acid and at least one acrylate based carboxyl-free olefinically unsaturated monomer.
25. A coating/paint composition comprising waterborne acrylated alkyd
dispersion comprising amine neutralized acrylic modified alkyd resin obtained of
copolymerizing

(I) at least one acrylic based unsaturated carboxylic acid and at least one acrylate
based carboxyl-free olefinically unsaturated monomer premixed with a free
radical initiator; in presence of
(II) alkyd resin comprising polycondensed product involving (a) about 40 to 80
weight percent of a vegetable oils or monobasic fatty acid,
(b) about 10 to 30 weight percent of a glycol or polyol,
(c) about 3 to 10 weight percent of a polyoxyethylene glycol,
(d) about 10 to 40 weight percent of a polycarboxylic acid.

26. A coating/paint composition as claimed in anyone of claims 23-25 having low
VOC content of less than 8% and broader particle size distribution (bimodel) of
50-1000 nm favouring gloss on both porous and non porous substrates; slow
drying for high gloss for brush applications.

27. A commercial or industrial material, a structure or building or a substrate
both porous and non-porous comprising coating/paint composition as claimed in
anyone of claims 23-25 having low VOC content of less than 8% and broader
particle size distribution (bimodel) of 50-1000 nm favouring gloss on both porous
and non porous substrates.

28. A method of coating/painting a commercial or industrial material, structure
or building or substrate both porous and non-porous comprising
selectively applying coating/paint composition as claimed in anyone of claims 23-
25 to atleast a portion of commercial or industrial material, a structure or building
or a substrate requiring low VOC (volatile organic compound) content, slow
drying and high gloss coats/paints.
AMENDED CLAIMS
received by the International Bureau on 04 April 2014 (04.04.2014)

We Claim:

1. Alkyd resin comprising a polycondensed product obtained of
(a) 40 to 80 weight percent of a vegetable oils or monobasic fatty acid,
(b) 10 to 30 weight percent of a glycol or polyol,
(c) 3 to 10 weight percent of a polyethoxypolyol
(d) 10 to 40 weight percent of a polycarboxylic acid.

2. Alkyd resin as claimed in claim 1 comprising said polycondensed product having
high molecular weight by low viscosity, involving viscosity values ranging from U to
Z1 at 25 °C on Gardner scale (at 90% solids in glycol ether) with a number average
molecular weight (Mn) of 1500 to 4000 and weight average molecular wt. (Mw) 8000
to 20000 and a final acid value less than 5 mg-KOH/g on solids and low
polydispersity index (PDI) of less than 4 and Gardner-Holdt viscosity in the range of
W to Y at > 90.0% non-volatiles in glycol ether based solvents to achieve good
stability.

3. Alkyd resin as claimed in anyone of claims 1-2, comprising said polycondensed
product adapted for modification by co-polymerization at substantially low co-solvent
of <10 percent to achieve good hydrolysis resistance.

4. A process for the preparation of alkyd resin as claimed in anyone of claims 1-3
comprising said polycondensed product comprising the steps of
(a) polycondensing a selective mix comprising 40 to 80 weight percent vegetable
oils or monobasic fatty acid, 10 to 30 weight percent glycol or polyol, 3 to 10 weight
percent polyethoxypolyol, and 10 to 40 weight percent of polycarboxylic acid at
reaction temperature of up to 245°C;
(b) continuing the polycondensation reaction until a final acid value of the resultant
alkyd resin of <5 on solids is reached.

5. A process as claimed in claim 4 wherein said step (b) comprises the steps of
(i) polycondensing the selective mix to an acid number in the range of 15 to 60 mg-
KOH/g preferably 31 mg-KOH/g initially in the temperature range of 200 to 260 °C
preferably 238°C over a period of 1 to 4 hours preferably 2 hours;
(ii) attaining a maximum temperature preferably 245°C at the acid value of preferably 4.5;
(iii) continuing the condensation reaction until the attainment of acid value in the range of 1 to 10 mg-KOH/g preferably 2.9 that is followed by cooling to discharge the resultant alkyd resin that is clear and free from suspended matters with non volatiles in the range of 90 to 100% preferably 97.1% and having a final acid value in the range of 1 to 10 mg-KOH/g preferably 2.5 mg-KOH/g.

6. A waterborne acrylated alkyd dispersion comprising amine neutralized acrylic modified alkyd resin involving
(a) 40 to 80 weight percent of a vegetable oils or monobasic fatty acid,
(b) 10 to 30 weight percent of a glycol or polyl,
(c) 3 to 10 weight percent of a polyethoxypolyol,
(d) 10 to 40 weight percent of a polycarboxylic acid;
(e) 15-40 weight percent at least one acrylic based unsaturated carboxylic acid and at least one acrylate based carboxyl-free olefinically unsaturated monomer.

7. A waterborne acrylated alkyd dispersion comprising amine neutralized acrylic modified alkyd resin obtained of copolymerizing
(i) 15-40 weight percent of at least one acrylic based unsaturated carboxylic acid and at least one acrylate based carboxyl-free olefinically unsaturated monomer; in presence of
(ii) polycondensed product involving (a) 40 to 80 weight percent of a vegetable oils or monobasic fatty acid, (b) 10 to 30 weight percent of a glycol or polyl, (c) 3 to 10 weight percent of a polyethoxypolyol, (d) 10 to 40 weight percent of a polycarboxylic acid.

8. A waterborne acrylated alkyd dispersion as claimed in anyone of claims 6 or 7 which is having a low VOC (volatile organic compound) content of less than 8% and broader particle size distribution (bimodel) of 50-1000 nm.

9. A waterborne acrylated alkyd dispersion as claimed in anyone of claims 6 to 8 having a Gardner-Holdt viscosity in the range of from Z1 to Z5, at 40-50% non-volatiles at room temperature and a number average molecular weight (Mn) of 3000-4500 and weight average molecular wt. (Mw) 30000-150000.
10. A waterborne acrylated alkyd dispersion as claimed in anyone of claims 6 to 9 comprising 10-40% of particle having average particle size in the range of 350-600 nm, and 60-90% of particles having average particle size in the range of 30-200 nm.

11. A waterborne acrylated alkyd dispersion as claimed in anyone of claims 6 to 10 that is substantially free of volatile organic solvents and exhibits a long shelf life and storage stability for 30 days at 55 °C, a high shear stability of 2500 rpm speed virtually with no aggregate formation, high wet-film stability of 18 hrs, increased open time of 30-45 minutes and wherein dispersions with particle sizes even upto 1 µm remains stable and free from gel specks despite being substantially free from organic solvents.

12. A waterborne acrylated alkyd dispersion as claimed in anyone of claims 6 to 11 wherein said at least one acrylic based unsaturated carboxylic acid is preferably methacrylic acid and at least one acrylate based carboxyl-free olefinically unsaturated monomer is preferably selected from methyl methacrylate, butylmethacrylate, ethylmethylacrylate, tertiarybutylmethacrylate, isobutylmethacrylate, hydroxyethylmethacrylate, hydroxypropylmethacrylate.

13. A waterborne acrylated alkyd dispersion as claimed in anyone of claims 6 to 12 comprising monobasic fatty acid selected from the formulas represented hereunder:

\[
\begin{align*}
\text{R} &= \text{Linoleic} \\
\text{R} &= \text{Linolenic} \\
\end{align*}
\]
and includes sunflower oil, canola oil, dehydrated castor oil, coconut oil, corn oil, cottonseed oil, fish oil, linseed oil, oiticica oil, soya oil, and tung oil, animal grease, castor oil, lard, palm kernel oil, peanut oil, perilla oil, safflower, tallow oil, walnut oil and are preferably selected from fatty acid components of oil or fatty acids including oil derived fatty acids of tallow acid, linoleic acid, linolenic acid, oleic acid, soya acid, myristic acid, linseed acid, crotonic acid, versatic acid, coconut acid, tall oil fatty acid, rosin acid, neodecanoic, neopentanoic, isostearic, 12-hydroxystearic, cottonseed acid with linoleic, linolenic more preferably oleic.

14. A waterborne acrylated alkyd dispersion as claimed in anyone of claims 6 to 13 comprising glycol or polyol including aliphatic, alicyclic, and aryl alkyl glycols and are preferably selected from ethylene glycol; propylene glycol; diethylene glycol; triethylene glycol; tetraethylene glycol; pentaethylene glycol; hexaethylene glycol; heptaethylene glycol; octaethylene glycol; nonaethylene glycol; decaethylene glycol; 1,3-propanediol; 2,4-dimethyl-2-ethyl-hexane-1,3-diol; 2,2-di methyl-1,2-propanediol; 2-ethyl-2-butyl-1,3-propanediol; 2-ethyl-2-isobutyl-1,3-propanediol; 1,3-butanediol; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; 2,2,4-tetramethyl-1,6-hexanediol; thiodiethanol; 1,2-cyclohexanediethanol; 1,3-cyclohexanedi methanol; 1,4-cyclohexanedimethanol; 2,2,4-trimethyl-1,3-pentanediol; 2,2,4-tetramethyl-1,3-cyclobutanediol; p-xylenedi hydroxypivalyl hydroxypivalate; 1,10-decanediol; hydrogenated bisphenol A; trimethylolpropane; trimethylolethane; pentaerythritol; erythritol; threitol; dipentaerythritol; sorbitol; glycerine; trimellitic anhydride; pyromellitic dianhydride; dimethylolpropionic acid.

15. A waterborne acrylated alkyd dispersion as claimed in anyone of claims 6 to 14 comprising polyethoxypolyol selected from polyethoxypolyol 400, polyethoxypolyol 600, polyethoxypolyol 1000, polyethoxypolyol 2000.

16. A waterborne acrylated alkyd dispersion as claimed in anyone of claims 6 to 15 comprising polycarboxylic acid selected from isophthalic acid, terephthalic acid, phthalic anhydride(acid), adipic acid, tetrachlorophthalic anhydride, dodecanedioic acid, sebacic acid, azelaic acid, 1,4-cyclohexanedicarboxylic acid, 1,3-
cyclohexanedicarboxylic acid, maleic anhydride, fumaric acid, succinic anhydride(acid), 2,6-naphthalenedicarboxylic acid, glutaric acid and esters thereof.

17. A waterborne acrylated alkyd dispersion as claimed in anyone of claims 6 to 16 that is amine neutralized with volatile amines to form salts selected from primary amines including ethyl amine, propyl amine, butyl amine, isoamyl amine, amyl amine, hexyl amine, heptyl amine and ethanol amine; secondary amines including diethyl amine, ethyl ethanol amine, and morpholine; and tertiary amines including dimethylethanol amine, trimethyl amine, triethylamine and N-methyl morpholine.

18. A process for the preparation of a waterborne acrylated alkyd dispersion as claimed in anyone of claims 6 to 17 comprising said amine neutralized acrylic modified alkyd resin comprising reacting
(a) 40 to 80 weight percent of a vegetable oils or monobasic fatty acid,
(b) 10 to 30 weight percent of a glycol or polyol,
(c) 3 to 10 weight percent of a polyethoxypolyol ,
(d) 10 to 40 weight percent of a polycarboxylic acid; and
(e) 15-40 weight percent at least one acrylic based unsaturated carboxylic acid and at least one acrylate based carboxyl-free olefinically unsaturated monomer; and obtaining therefrom said waterborne acrylated alkyd dispersion.

19. A process for the preparation of a waterborne acrylated alkyd dispersion comprising amine neutralized acrylic modified alkyd resin as claimed in anyone of claims 6 to 17 comprising the steps of:

(I) providing said alkyd resin comprising said polycondensed product involving (a) 40 to 80 weight percent of a vegetable oils or monobasic fatty acid,
(b) 10 to 30 weight percent of a glycol or polyol,
(c) 3 to 10 weight percent of a polyethoxypolyol,
(d) 10 to 40 weight percent of a polycarboxylic acid ;
(II) copolymerizing at least one acrylic based unsaturated carboxylic acid and at least one acrylate based carboxyl-free olefinically unsaturated monomer premixed with a free radical initiator in the presence of said alkyd resin of step (I) and neutralizing with amine; to finally obtain therefrom said waterborne acrylated alkyd dispersion.
20. A process as claimed in claim 19 wherein said copolymerization step (II) preferably comprises the steps of:
(i) premixing at least one acrylate based carboxyl-free olefinically unsaturated monomer involving non-carboxylic acid vinyl monomers and at least one acrylic based unsaturated carboxylic acid involving vinyl carboxylic acid preferably methacrylic acid with a free radical initiator;
(ii) slowly adding the premix to the selective alkyd in ratios ranging from 85:15 to 70:30 in the temperature range of 130-140°C for a time period of 1 - 4 hrs preferably 2 hrs for a high degree of conversion of said non-carboxylic acid vinyl and vinyl carboxylic acid monomers so as to reach to the copolymer acid value of 30-60 on solids;
(iii) neutralizing the carboxylic acids end groups with various amines followed by thinning with water to obtain said waterborne acrylated alkyd dispersion.

21. A coating/ paint composition comprising waterborne acrylated alkyd dispersion comprising amine neutralized acrylic modified alkyd resin obtained of copolymerizing (I) at least one acrylic based unsaturated carboxylic acid and at least one acrylate based carboxyl-free olefinically unsaturated monomer premixed with a free radical initiator; in presence of
(II) alkyd resin comprising polycondensed product involving (a) 40 to 80 weight percent of a vegetable oils or monobasic fatty acid,
(b) 10 to 30 weight percent of a glycol or polyol,
(c) 3 to 10 weight percent of a polyethoxypolyol,
(d) 10 to 40 weight percent of a polycarboxylic acid,

22. A coating/ paint composition as claimed in claim 21 having low VOC content of less than 8% and broader particle size distribution (bimodel) of 50-1000 nm favouring gloss on both porous and non porous substrates; slow drying for high gloss for brush applications.
23. A commercial or industrial material, a structure or building or a substrate both porous and non-porous comprising coating/paint composition as claimed in anyone of claims 21-22 having low VOC content of less than 8% and broader particle size distribution (bimodel) of 50-1000 nm favouring gloss on both porous and non porous substrates.

24. A method of coating/painting a commercial or industrial material, structure or building or substrate both porous and non-porous comprising selectively applying coating/paint composition as claimed in anyone of claims 21-22 to atleast a portion of commercial or industrial material, a structure or building or a substrate requiring low VOC (volatile organic compound) content, slow drying and high gloss coats/paints.
STATEMENT UNDER ARTICLE 19 OF PCT

Amended claims are directed to further clarify and qualify the advancement residing in the alkyd resin, the waterborne acrylated alkyd dispersion and the coating/paint composition comprising the said dispersion and their processes of manufacture wherein the alkyd resin of the present advancement has been specifically limited to include only polyethoxypolyol demonstrated in working Example 1A that surprisingly and unexpectedly aids in achieving the desired attributes of a polycondensed product alkyd having a highly branched structure with a low viscosity and high molecular weight and yet good dispersibility in water of both the alkyd and the corresponding acrylic modified alkyds.

The amendments in the claims are directed to qualify the claimed invention and do not extend beyond the disclosure and directions in the international application as filed.
## A. CLASSIFICATION OF SUBJECT MATTER

According to International Patent Classification (IPC) or to both national classification and IPC

### ADD.

INV. C09D167/00 C08G63/00 C09D133/00

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09D C09G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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**Date of the actual completion of the international search**

19 November 2013

**Date of mailing of the international search report**

27/11/2013

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk
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Lauteschlaeger, S
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